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Shelf-life prediction of olive oils using empirical models developed at low and high temperatures

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ABSTRACT

Induction period of the formation of hydroperoxides and conjugated dienes at 50 °C and oxidative stability index at 100–130 °C as the oxidative stability measures of different types of olive oils with a wide range of chemical compositions were determined. Regression models ($R^2 \geqslant 0.95$) developed at low and high temperatures showed different contributions of compositional variables (the ratio between monounsaturated and polyunsaturated fatty acids, the content of total tocopherols and phenolics, peroxide value, acid value, and total polar compounds content) to the oxidative stability measures. To estimate the shelf-life of olive oils at low temperature, three empirical models with errors of ±1.5%, <±10%, and ±21.2% were developed.

1. Introduction

High oxidative and nutritional quality of olive oils has made their volume of global trade grow increasingly at the present time. One of the matters of great importance for producers and consumers is undoubtedly the maintenance and assurance of the olive oils quality throughout the commercial period. Autoxidation, which lead to loss of nutritional value and to form a series of off-flavour and rancidity compounds in edible fats and oils, is the main cause of deterioration in the olive oils quality and its reaction rate determines the oxidative stability or shelf-life of these products (Frankel, 1998).

Autoxidation reaction occurs fairly slowly at ambient conditions, and therefore accelerated stability tests should be employed to determine the oxidative stability or shelf-life of olive oils. Temperature is the most usual parameters chosen to accelerate the autoxidation reaction, because it increases the rate of the reaction exponentially (Frankel, 1998). It has been reported a few limited studies on the oxidation kinetics of olive oil triacylglycerols (Gomez-Alonso, Mancebo-Campos, Salvador, & Fregapane, 2004; Gomez-Alonso, Salvador, & Fregapane, 2004) and on the shelf-life estimation of a monovarietal extra virgin olive oil at storage temperatures below 60 °C (Mancebo-Campos, Fregapane, & Salvador, 2008). Since the mechanism of lipid oxidation changes with temperatures above 60 °C (Frankel, 1993), no marked success has ever been achieved in the shelf-life prediction of edible fats and oils by the conventional accelerated stability tests (e.g. Rancimat and AOM, active oxygen method) which are often run at temperatures of at least 100 °C.

The shelf-life of edible fats and oils at ambient conditions has been estimated by plotting the logarithm of oxidative stability results versus high temperatures and extrapolating to room temperature. It has been shown that extrapolation from the Rancimat values (oxidative stability index, OSI) to ambient conditions lead to either over-prediction or under-prediction of the actual shelf-life depending on the fatty acid composition of the oils (Kaya, Tekin, & Oner, 1993). This has been attributed to the fact that the Rancimat test estimates the shelf-life of much more oxidised oils than other storage tests run between 40 and 60 °C (Frankel, 1998). Nevertheless, the calculation of an average extent of over- and/or under-prediction for each oil type and considering it to the shelf-life value resulted from extrapolating to ambient conditions may provide acceptable results to some extent.

In a previous research on canola oil oxidation at 180 °C (Farhoosh & Pazhouhanmehr, 2009), regression models with high correlation coefficients ($R^2 > 0.95$) were developed to determine the relative contribution of three sets of compositional variables, including fatty acid composition, indigenous antioxidative compounds (the content of total tocopherols, TT, and phenolic compounds, TP), and initial quality indicators (peroxide value, PV, acid value, AV, and the content of total polar compounds, TPC) to the oxidative stability measures based on the changes in the values of carbonyls (CV) and conjugated dienes (CDV). Development of a low-temperature regression model for different types of olive oils with a wide range of chemical compositions may be considered

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to be a suitable approach to estimate the olive oils shelf-life using the chemical composition data. In addition, an interrelated mathematical equation of the low- and high-temperature regression models, if possible to develop, will provide shelf-life estimation from the accelerated stability results.

This paper reports research into the oxidative stability of different types of olive oils with a wide range of chemical compositions at low (induction period, IP, of the formation of hydroperoxides and conjugated dienes at 50 °C) and high (the OSI value at 100–130 °C) temperatures. Attempts were made to develop some regression models to establish the relationship between oxidative stability measures (the IP or OSI values) and the compositional variables. Finally, the olive oils shelf-life at mild storage conditions was estimated by the empirical models developed in this study.

2. Materials and methods

2.1. Materials

Nine olive oil samples of different brands in 1 l glass bottles were purchased from local shops and were stored at 4 °C until analysis. Fatty acid methyl ester (FAME) standards, and all chemicals and solvents used in this study were of analytical reagent grade and supplied by Merck and Sigma Chemical Companies.

2.2. Accelerated stability test

A Metrohm Rancimat model 743 (Herisau, Switzerland) was used to measure the OSI of olive oil samples. The tests were carried out with 3 g of the oil samples at temperatures of 100, 110, 120, and 130 °C at an airflow rate of 25 l/h.

2.3. Storage stability test

Olive oil samples (60 g) were stored in darkness at 50 °C in 130 ml open amber glass bottles (i.d.: 4.6 cm; surface area exposed to the air: 18.5 cm^2). Samples were taken from the incubator for analysis at scheduled times.

2.4. Fatty acid composition

The fatty acid composition of the oils was determined by gas–liquid chromatography and was reported in relative area percentages. Fatty acids were transesterified into their corresponding FAMEs by vigorous shaking of a solution of oil in hexane (0.3 g in 7 ml) with 2 ml of 7 N methanolic potassium hydroxide at 50 °C for 10 min. The FAMEs were identified using an HP-5890 chromatograph (Hewlett–Packard, CA, USA) equipped with a CP-FIL 88 (Supel Co., Inc., Bellefonte, PA, USA) capillary column of fused silica, 60 m in length × 0.22 mm I.D., 0.2 μm film thickness, and a flame ionisation detector (FID). Nitrogen was used as carrier gas with a flow rate of 0.75 ml min^{-1}. The oven temperature was maintained at 198 °C, and that of the injector and the detector at 250 °C (Farhoosh, Niazmand, Rezaei, & Sarabi, 2008).

2.5. Peroxide value (PV)

The spectrophotometric method described by Shantha and Decker (1994) was used to determine the PV. The oil samples (⩽0.01–0.30 g, depending on the extent of peroxidation) was mixed in a disposable glass tube with 9.8 ml chloroform–methanol (7:3 v/v) on a vortex mixer for 2–4 s. Ammonium thiocyanate solution (50 ml, 30% w/v) was added and the sample was mixed on a vortex mixer for 2–4 s. Then, 50 ml of iron (II) chloride solution ([0.4 g barium chloride dihydrate dissolved in 50 ml H2O] + [0.5 g FeSO4·7H_2O dissolved in 50 ml H_2O] + 2 ml 10 M HCl, with the precipitate, barium sulphate, filtered off to produce a clear solution]) was added, and the sample was mixed on a vortex mixer for 2–4 s. After 5 min incubation at room temperature, the absorbance of the sample was read at 500 nm against a blank that contained all the reagents except the sample by using a spectrophotometer. The entire procedure was conducted in subdued light and completed within 10 min. Results were expressed in milliequivalents of oxygen per kilogram of oil.

2.6. Acid value (AV)

The AV was determined according to the AOCS. (1993). For the AV determination, titration of the oil samples (10 g) dissolved in 50 ml of previously neutralised chloroform–ethanol medium (50:50 v/v) was applied, using an ethanolic solution of 0.1 N potassium hydroxide (KOH) as the standard reagent to a phenolphthalein endpoint. The AV value was expressed as milligrams of KOH required to neutralise the free fatty acids present in 1 g of the oil sample (mg g^{-1}).

2.7. Total tocopherols (TT) content

The TT content was determined according to the colorimetric method described by Wong, Timms, and Goh (1988). A calibration

Table 1
Chemical composition data and oxidative stability indices (OSI, h) of the olive oil samples.[a]

Oil	M/P[b] ratio	PV[c]	AV[d]	TPC[e]	TT[f]	TP[g]	OSI at			
							100 °C	110 °C	120 °C	130 °C
1	5.0 f	4.9 e	0.7 d	14.6 a	222.0 c	45.1 cd	29.7 dA	12.6 eB	6.5 cC	2.8 cdD
2	5.6 e	16.8 ab	4.2 a	8.1 ce	312.3 b	144.9 a	30.5 dA	13.1 eB	6.0 cdC	2.6 cdD
3	6.4 c	8.1 d	1.0 c	7.2 df	321.3 b	94.2 b	37.7 bA	15.2 cB	6.5 cC	2.9 cD
4	7.8 b	10.6 c	4.4 a	8.2 c	99.8 h	57.7 c	15.6 fA	6.9 fB	3.4 fC	1.6 eD
5	4.0 g	9.0 d	0.6 e	8.6 c	164.8 g	51.8 c	21.8 eA	9.1 eB	4.3 eC	1.9 eD
6	9.2 a	17.0 a	2.9 b	10.4 b	186.9 f	86.1 b	30.7 dA	14.1 dB	5.9 dC	2.7 cD
7	8.2 b	15.6 b	0.9 c	7.0 edf	485.6 a	151.4 a	55.1 aA	24.2 aB	11.2 aC	5.0 aD
8	6.0 d	5.7 e	0.2 f	6.9 f	204.9 d	26.0 e	34.6 cA	14.4 dB	6.5 cC	3.1 cD
9	9.1 a	3.0 f	0.3 f	9.9 b	198.1 e	27.7 de	39.8 bA	18.2 bB	8.5 bC	3.9 bD

[a] All values are means of three determinations with coefficient of variations <8%. Means within a column with the same lowercase letters are not significantly different at $P < 0.05$. Means within a row with the same uppercase letters are not significantly different at $P < 0.05$.
[b] The ratio between monounsaturated fatty acids (%) and polyunsaturated fatty acids (%).
[c] Peroxide value (meq O_2 per kg oil).
[d] Acid value (mg KOH per g oil).
[e] Total polar compounds content (%).
[f] Total tocopherols content (mg α-tocopherol per kg oil).
[g] Total phenolics content (mg gallic acid per kg oil).